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COUPLED-OSCILLATOR NATURAL ORBITALS

Peter D. Robinson

Mathematics Research Center
University of Wisconsin—Madison
610 Walnut Street
Madison, Wisconsin 53706

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ABSTRACT

The natural orbitals are derived for a pair of identical coupled harmonic oscillators in their ground state.

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Key Words: Natural orbitals, Coupled harmonic oscillators, Integral operator, Eigenvectors

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COUPLED-OSCILLATOR NATURAL ORBITALS

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Examples of natural orbitals in closed form seem rare enough [1] to justify this note, in which such orbitals are exhibited for coupled oscillators.

Let $\{\theta_n(\alpha, x)\}$ denote the complete set of orthonormal eigenfunctions of the oscillator Hamiltonian

$$h(\alpha, x) = -\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}\alpha^4 x^2, \quad \alpha > 0, \quad -\infty < x < \infty \quad , \tag{1}$$

corresponding to the eigenvalues $(n + \frac{1}{2})\alpha^2$. Specifically

$$\theta_n(\alpha, x) = \left[\frac{\alpha}{\pi^{\frac{1}{2}} 2^n n!}\right]^{\frac{1}{2}} H_n(\alpha x) \exp(-\frac{1}{2}\alpha^2 x^2), \quad n = 0, 1, 2 \ldots \quad , \tag{2}$$

where the Hermite polynomials $H_n(\alpha x)$ are orthogonalized with respect to a weight factor [2] $\exp(-\alpha^2 x^2)$. Consider now the identical coupled oscillators described by the Hamiltonian

$$H = -\frac{1}{2}\frac{d^2}{dx_1^2} - \frac{1}{2}\frac{d^2}{dx_2^2} + \frac{1}{2}a^4(x_1^2 + x_2^2) - \frac{1}{4}(a^4 - b^4)(x_1 - x_2)^2 \, ,$$

$$a > b > 0, \quad -\infty < x_1 < \infty, \quad -\infty < x_2 < \infty \, . \tag{3}$$

In terms of the coordinates

$$y_1 = \frac{1}{\sqrt{2}}(x_1 + x_2), \quad y_2 = \frac{1}{\sqrt{2}}(x_1 - x_2) \, , \tag{4}$$

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the Hamiltonian (3) takes the separable form

$$H = h(a,y_1) + h(b,y_2) . \tag{5}$$

The ground-state wave-function thus has a space part

$$\begin{aligned}\psi(x_1,x_2) &= \theta_0(a,y_1)\theta_0(b,y_2) = \left(\frac{ab}{\pi}\right)^{\frac{1}{2}} \exp(-\tfrac{1}{2}a^2y_1^2 - \tfrac{1}{2}b^2y_2^2) \\ &= \left(\frac{ab}{\pi}\right)^{\frac{1}{2}} \exp\{-\tfrac{1}{4}(a^2+b^2)(x_1^2+x_2^2) - \tfrac{1}{2}(a^2-b^2)x_1x_2\} ,\end{aligned} \tag{6}$$

which is the eigenfunction of the operator (5) corresponding to the eigenvalue $\frac{1}{2}(a^2 + b^2)$.

This function $\psi(x_1,x_2)$ is symmetric in x_1 and x_2, and is normalized so that

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^2 dx_1 dx_2 = 1 . \tag{7}$$

Accordingly, $\psi(x_1,x_2)$ is the Hilbert-Schmidt-type kernel of a compact, self-adjoint integral operator on the real Hilbert space $L_2(-\infty,\infty)$. Standard integral equation theory [3] tells us that this operator has a complete orthonormal set of eigenvectors $\{\phi_n\}$ defined by

$$\int_{-\infty}^{\infty} \psi(x_1,x_2)\phi_n(x_2)dx_2 = \lambda_n\phi_n(x_1), \quad n = 0,1,2... , \tag{8}$$

with the eigenvalues λ_n accumulating at zero. Further, the expansion

$$\frac{1}{2}\gamma(x_1,x_2) = \int_{-\infty}^{\infty} \psi(x_1,s)\psi(x_2,s)ds = \sum_{n=0}^{\infty} \lambda_n^2\phi_n(x_1)\phi_n(x_2) \tag{9}$$

is convergent for all x_1 and x_2. The functions $\phi_n(x)$ are precisely the natural orbitals for $\psi(x_1,x_2)$, and (9) gives the expansion for the first-order density matrix $\gamma(x_1,x_2)$. The "occupation numbers" λ_n^2 must sum to unity, from (7) and (9). The expansion for $\psi(x_1,x_2)$ itself, namely

$$\psi(x_1,x_2) \sim \sum_{n=0}^{\infty} \lambda_n \phi_n(x_1)\phi_n(x_2) , \tag{10}$$

must also be convergent, at least in the L_2 norm sense.

In the case of the function given in (6), the expansion (10) can be found directly, and is convergent for all x_1 and x_2. Mehler's formula [2] states that

$$\exp\left\{-\frac{z^2}{1-z^2}(t_1^2+t_2^2)+\frac{2z}{1-z^2}t_1t_2\right\} = (1-z^2)^{\frac{1}{2}}\sum_{n=0}^{\infty}\frac{z^n}{2^n n!}H_n(t_1)H_n(t_2),$$

$$-1 < z < 1,\ -\infty < t_1 < \infty,\ -\infty < t_2 < \infty . \tag{11}$$

Setting $t_1 = \alpha x_1$, $t_2 = \alpha x_2$ and multiplying through by $\exp\{-\frac{1}{2}\alpha^2(x_1^2+x_2^2)\}$, we obtain from (2):

$$\frac{\alpha}{\pi^{\frac{1}{2}}}\exp\left\{-\left(\frac{1+z^2}{1-z^2}\right)\frac{\alpha^2}{2}(x_1^2+x_2^2)+2\frac{\alpha^2 z}{1-z^2}x_1x_2\right\} = (1-z^2)^{\frac{1}{2}}\sum_{n=0}^{\infty} z^n\theta_n(\alpha,x_1)\theta_n(\alpha,x_2). \tag{12}$$

With the choices

$$\alpha = (ab)^{\frac{1}{2}},\ z = -\frac{a-b}{a+b} \tag{13}$$

the left-hand side of (12) becomes $\psi(x_1,x_2)$ as given in (6). Thus

$$\psi(x_1, x_2) = \sum_{n=0}^{\infty} \left\{ \frac{2\sqrt{ab}}{a+b} (-1)^n \left(\frac{a-b}{a+b} \right)^n \right\} \theta_n(\sqrt{ab}, x_1) \theta_n(\sqrt{ab}, x_2) , \tag{14}$$

so that for the ground-state of the coupled oscillators we have the natural orbitals

$$\phi_n(x) = \theta_n(\sqrt{ab}, x) = \left[\frac{\sqrt{ab}}{\pi^{\frac{1}{2}} 2^n n!} \right]^{\frac{1}{2}} H_n(\sqrt{ab}\, x) \exp(-\tfrac{1}{2} ab\, x^2) , \tag{15}$$

and corresponding eigenvalues

$$\lambda_n = \frac{2\sqrt{ab}}{a+b} (-1)^n \left(\frac{a-b}{a+b} \right)^n . \tag{16}$$

The orbitals (15), and the occupation numbers λ_n^2, can also be obtained by working from the expression for $\frac{1}{2}\gamma(x_1, x_2)$, which is

$$\frac{1}{2}\gamma(x_1, x_2) = ab\left[\frac{\pi}{2}(a^2 + b^2) \right]^{-\frac{1}{2}} \exp\left\{ - \frac{(a^4 + b^4 + 6a^2b^2)}{8(a^2 + b^2)} (x_1^2 + x_2^2) + \frac{(a^2 - b^2)^2}{4(a^2 + b^2)} x_1 x_2 \right\} . \tag{17}$$

Extension to three-dimensional oscillators, for which Davidson [1] has discussed the first-order density matrix, is straightforward.

REFERENCES

1. E. R. Davidson, Reduced Density Matrices in Quantum Chemistry, (Academic Press) 1976.
2. A. Erdélyi (Ed.), Higher Transcendental Functions, II, Ch. 10, (McGraw-Hill) 1953.
3. R. Courant and D. Hilbert, Methods of Mathematical Physics, I, (Interscience) 1953.

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